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# A Thin Film Degradation Study of a Fluorinated Polyether Liquid Lubricant Using an HPLC Method

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STUDY OF A FLUORINATED POLYETHER LIQUID  
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**NASA**



A THIN FILM DEGRADATION STUDY OF A FLUORINATED POLYETHER  
LIQUID LUBRICANT USING AN HPLC METHOD

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Abstract

An HPLC separation method was developed to study and analyze a fluorinated polyether fluid which is a promising liquid lubricant for future applications. This HPLC separation method was used in a preliminary study investigating the catalytic effect of various metal, metal alloy, and ceramic engineering materials on the degradation of this fluid in a dry air atmosphere at 345 °C. Using 440C stainless steel as a reference catalytic material it was found that a titanium alloy and a chromium plated material degraded the fluorinated polyether fluid substantially more than the reference material.

INTRODUCTION

Fluorinated polyethers are a relatively new generation of fluids which possess special properties that make them a promising class of liquid lubricants for use aboard advance aircraft and spacecraft. Advanced aircraft will require lubricants and hydraulic fluids with high thermal and oxidative stability; maximum fluid temperatures in excess of 316 °C have been estimated for future applications (1-4). Spacecraft will require lubricants with extremely low vapor pressures to minimize evaporation loss.

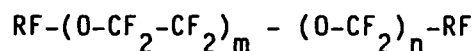
One particular fluorinated polyether (basically a relatively low molecular weight unbranched perfluoroalkylether polymer) exhibits the following properties: excellent thermal and oxidative stability (5,6), a very low pour point and volatility, good boundary lubricating ability, chemical inertness and nonflammability properties, and high radiation resistance. Because of its

extremely low vapor pressure this fluorinated polyether fluid is being used as a lubricant in instrument ball bearing units aboard several satellites.

Since this fluid is a promising candidate for future high temperature lubrication applications, knowledge of its compatibility with common metals, metal alloys, and ceramic engineering materials is needed (some preliminary work in this area has been reported (7)), and a means of analyzing this and other fluorinated fluids is essential. The purpose of this study is twofold: (1) to develop a high pressure liquid chromatography (HPLC) method to analyze the fluorinated polyether fluid and its decomposition products, and (2) to use this HPLC method in a preliminary study on the effect of various materials on the degradation of a thin film of the fluorinated polyether in a dry air atmosphere at 345 °C.

#### EXPERIMENTAL FLUID SAMPLE

The fluorinated polyether used in this study is a fluid, having an average molecular weight of 9500, with the following general formula:



where RF designates inert fluorinated groups.

Table 1 lists some of the fluid's typical properties. This fluid is water repellent, biologically inert, and is synthesized from the photo-oxidation of fluoro-olefins (8).

#### EXPERIMENTAL APPARATUS

##### Thin Film Oxidation Apparatus

The fluorinated polyether fluid was tested using a thin film oxidation apparatus (Fig. 1) which was originally developed at Penn State University (9). The concept behind the thin film oxidation test is to study a fluid's thermal oxidative stability in a short time period (not more than 30 min), under thin film (<0.5 mm) conditions; conditions where there exists a large catalytic

solid surface area to fluid volume ratio so that temperature and concentration gradients across the thin fluid film are minimized.

The original Penn State University thin film oxidation apparatus consisted only of the reactor glass unit, which sat inside a temperature controlled heated section, where a continuous flow (20 ml/min) of air or nitrogen purged the unit during a test. In this study a modification was made to the original apparatus; a second glass unit (called the collector unit) was attached to the reactor unit to allow the purging air or nitrogen gas to flow into a fluorinated solvent reservoir (10 ml) at room temperature. This should permit the dissolving of any volatile decomposition products into the solvent. This collector unit thus allows the collection and storage of the solvent reservoir for analysis of possible volatile decomposition products.

Table 2 lists the metal, metal alloy, and ceramic materials used in this study.

#### HPLC Method Development

Analysis of the fluorinated polyether sample, and its degradation products, was performed using HPLC in the size exclusion mode. The unit was combined with an ultraviolet, (UV) absorbance detector and a differential refractive index (RI) detector. The UV detector monitors the absorbance at a wavelength of 254 nm at sensitivities ranging from 0.005 to 2.000 absorbance units full scale (AUFS). The refractometer is sensitive to all compounds that differ in refractive index from the mobile phase. It will detect changes in the RI as small as  $10^{-7}$  units throughout the RI range of 1.00 to 1.75.

Previous research (10-12) involving hydrocarbon-based liquid lubricants, was performed using Styragel-based columns with chloroform as the mobile phase. It was found that chloroform could not dissolve the fluorinated polyether sample. Solubility testing revealed that the only common laboratory solvent capable of dissolving the fluorinated polyether sample, as well as other

fluorocarbon materials, was 1,1,2 trichlorotrifluoroethane, henceforth referred to as the fluorinated solvent or mobile phase. A second problem encountered was the incompatibility of the Styragel-based columns with the fluorinated solvent due to swelling of the Styragel packing. This problem was corrected by switching to size exclusion columns having silica-based packing which do not swell or shrink in the presence of the fluorinated solvent.

Two size exclusion calibration charts were constructed to assist in the analysis of the fluorinated polyether sample. Figure 2 is a molecular weight distribution chart relating the molecular weight of a size exclusion peak to its retention time. This chart was constructed by measuring the size exclusion retention time of a series of different fluorocarbon substances, and plotting the natural log of the molecular weight of each substance versus its retention time.

Figure 3 is a concentration chart relating the amount of fluorinated polyether sample detected to its peak height. This chart was constructed by injecting 30  $\mu$ l of a prepared fluorinated polyether sample, having a known concentration, into the HPLC unit, measuring the peak height of the resulting chromatogram, and subsequently plotting the known concentration values versus their peak heights.

#### TEST PROCEDURE

Each catalyst cup specimen was rinsed first with the fluorinated solvent and then with ethanol. This was followed by scrubbing the cup with a paste of alumina and rinsing off the paste with distilled, de-ionized water. The cup was then dried and placed into the bottom half of the thin film reactor unit. At room temperature, 50  $\mu$ l of the sample fluid (used "as is" from its glass container) was injected onto the cup surface. The entire thin film apparatus was then assembled and a nitrogen gas line was connected to the reactor unit gas inlet, with the nitrogen gas flow rate set at 50 ml/min.

After purging the apparatus for 30 min the nitrogen flow rate was reduced to 25 ml/min, and the reactor unit was placed into a preheated (345 ( $\pm$ 1) °C) oven. The reactor unit gas outlet was then connected to the gas inlet of the collector unit (Fig. 1) containing 10 ml of the fluorinated solvent.

The reactor unit was then heated at the set temperature for 10 min before switching the nitrogen gas flow to a dry air flow (<50 ppm water content) also set at 25 ml/min. After 30 min the air flow was switched back to nitrogen flow and the reactor unit was disconnected from the collector unit and removed from the oven. After the reactor was allowed to cool down to room temperature, 5 ml of the fluorinated solvent was injected into the bottom half of the reactor immersing the entire cup in the solvent. After a few minutes this solvent was drawn off, using a syringe, filtered through a 0.45  $\mu$ m nylon filter, and stored for HPLC analysis. The solvent from the collector unit was also filtered and stored for HPLC analysis.

For HPLC analysis the solvent flow rate was adjusted to 0.4 ml/min. Thirty  $\mu$ l of the solution withdrawn from the thin film reactor was injected into the HPLC unit and 100  $\mu$ l of the solution withdrawn from the collector unit were analyzed. For brevity, the solution collected from the reactor unit will be referred to as the "cup solution," and the solution withdrawn from the collector unit will be referred to as the "gaseous solution."

No UV absorbing material was detected for the entire study. Only refractive index changes will be reported.

## RESULTS AND DISCUSSION

The temperature chosen for this thin film study was based on the interaction of the fluorinated polyether fluid with a 440C stainless steel metal cup - which was selected as the reference catalyst material for this study. For a fixed test duration of 30 min, in a dry air atmosphere,

experimentation revealed that the fluorinated polyether fluid started to degrade at 345 °C.

The catalytic specimens used in this study represent a variety of engineering materials that may interact with the fluorinated polyether fluid at elevated temperatures. The use of the ceramic materials is an interesting one because of the continuing effort to incorporate ceramic components in high temperature systems such as the adiabatic diesel and gas turbine engines. The following results were obtained:

#### 440C Stainless Steel

Figure 4(a) is the size exclusion chromatogram of the cup solution. Two peaks are present, the sample peak at a 9.40 MRT (where MRT is an abbreviation for minutes retention time, the time it takes a solute to elute through the separatory columns), and a solvent peak at 14.40 MRT. The solvent peak is a characteristic elution peak due to the column-mobile phase setup; the solvent peak is analogous to the air peak of a GC separation. Based on the sample concentration chart (Fig. 3), the sample peak height correlates to a 19 percent loss of the original sample (All chromatographic data are  $\pm 5$  percent reproducible.).

Figure 4(b) is the size exclusion chromatogram of the gaseous solution. In addition to the solvent peak, a small peak eluded at 13.50 MRT. From the molecular weight calibration chart (Fig. 2) this retention time correlates to a 469 MW (where MW is an abbreviation for molecular weight). Visual inspection of the cup surface revealed the presence of small brownish deposits.

The thin film test was repeated under a continuous flow of dry nitrogen, and chromatographic analysis of the cup solution (Fig. 5) revealed a 4 percent loss of the original sample. No peaks were detected from the gaseous solution.



### Pure Iron

The results from the thin film test using a pure iron catalyst cup specimen show an 11 percent loss of the original cup sample (Fig. 6(a)). The gaseous solution chromatogram (Fig. 6(b)) shows an unknown peak at 13.50 MRT (469 MW) and inspection of the solvent peak reveals the existence of a shoulder which was not present in the previous chromatograms. The shoulder indicates the presence of a low molecular weight product. Visual inspection of the iron cup surface showed no deposit formation. These results indicate degradation of the sample fluid to lower molecular weight products.

### Chromium Plated Carbon Steel

The results for this thin film test (Fig. 7) show a 33 percent loss of the original cup sample and the appearance of a peak at 12.20 MRT (1261 MW). The gaseous solution chromatogram shows a low molecular weight peak at 13.20 MRT (584 MW). No deposit formation was visible on the cup surface. Like the iron catalyst cup thin film test the fluid seems to degrade to lower molecular weight products with no formation of a deposit on the cup surfaces. This is unlike the degradation of the fluid on the 440C cup surface where a small amount of lower molecular weight material was detected along with the brownish deposits.

### Titanium Alloy

A substantial loss of the fluid sample occurred using the titanium alloy cup specimen. The cup solution chromatogram (Fig. 8(a)) shows an 85 percent loss of the original sample with the detection of a lower molecular weight product at 12.60 MRT (944 MW), and a small asymmetric peak at a 18.10 MRT, well beyond the retention time of the solvent peak. This indicates separation due to adsorption effects between the solute and the column packing material (indicative of a polar solute) in addition to the size exclusion separation.



The gaseous solution chromatogram (Fig. 8(b)) shows the detection of three peaks, one at 13.00 MRT (682 MW), the second at 13.50 MRT (469 MW), and the third (the asymmetrical peak) at 18.10 MRT. A shoulder can be seen in the solvent peak. No deposits were observed on the cup surface. However, it was observed that the glassware used in this thin film test was visibly etched at the end of the test.

This thin film test was repeated in a dry nitrogen atmosphere where it was found that 5 percent of the original sample was lost (Fig. 9). No additional peaks were detected in the cup solution and no gaseous peaks were detected.

These results show the powerful catalytic effect the titanium alloy has on the degradation of the fluorinated polyether fluid in a dry air atmosphere at the test temperature of 345 °C. Not only was the sample fluid degraded 85 percent but the formation of lower molecular products was accompanied by the formation of a gaseous product that was capable of etching the glassware.

#### Copper

The cup solution chromatographic results for the thin film test with copper (Fig. 10) show a 2 percent fluid sample loss. No peaks were detected in the gaseous solution. Visible inspection of the copper cup surface showed tarnishing but no deposits were evident. The copper catalyst specimen seems to have no catalytic effect on the degradation of the fluorinated polyether fluid.

#### Zinc

The zinc cup solution chromatographic results (Fig. 11) show a 9 percent loss of the original sample with no formation of lower molecular weight products. The gaseous solution chromatogram only showed an increase in the peak height of the solvent peak with no shoulder present. No deposits were formed on the cup surface although the entire surface area of the zinc cup was tarnished with a milky film, evidently oxide formation.

### Brass Alloy

The results for this thin film test (Fig. 12) reveal a 5 percent loss of the original sample with no lower molecular weight product formation. The gaseous solution chromatogram showed no peak detection. No deposits were found on the brass cup surface but the surface was highly tarnished.

### Aluminum

Figure 13(a), the cup solution chromatogram, shows an 11 percent loss of the original sample with no secondary peak formation. The gaseous solution chromatogram (Fig. 13(b)) only reveals the presence of a shoulder on the solvent peak. No deposits were evident, and no tarnishing of the surface occurred.

The evidence seems to indicate that in the presence of the aluminum metal surface the fluorinated polyether fluid degrades to a lower molecular weight product, the shoulder on the solvent peak.

### Aluminum Oxide Ceramic

The chromatographic results for this thin film test using an aluminum oxide ceramic cup shows a 6 percent loss of the original sample (Fig. 14(a)). The gaseous sample chromatogram (Fig. 14(b)) shows a low molecular weight peak at 13.50 MRT (469 MW). No deposits were found on the ceramic cup surface.

### Zirconium Oxide Ceramic

The chromatographic results for this thin film test shows an 11 percent loss of the original sample with no secondary peak detection (Fig. 15(a)) using a zirconium oxide ceramic cup. The gaseous solution sample revealed the presence of a small peak at 13.00 MRT (682 MW) and the presence of a shoulder on the solvent peak (Fig. 15(b)).

Figure 16 summarizes the results of this study.

## CONCLUSIONS

The HPLC separation method (utilizing a fluorinated solvent as the mobile phase in conjunction with silica-based size exclusion columns), developed for the study of a candidate fluorinated polyether liquid lubricant, proved to be a practical means of detecting the sample fluid and its decomposition products. Its use in the high temperature thin film tests (studying the catalytic effects of various engineering materials on the degradation of the sample fluid in a dry air atmosphere at 345 °C) revealed that, in reference to the 440C stainless steel specimen, the titanium alloy and the chromium plated specimens proved to have the most detrimental catalytic effect on the sample fluid degradation. All the other cup specimens, including the ceramic specimens, were shown to be less catalytic on the degradation of the sample fluid.

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TABLE 1. - THE FLUORINATED POLYETHER PROPERTIES

Property	Test procedure	Typical value
Specific gravity	Mohr Westphal	1.8430 (20 °C)
Pour point	ASTM 97/66	-67 °C
Vapor pressure	Knudsen	$6 \times 10^{-13}$ torr (20 °C)
Kinematic viscosity	ASTM 445	250 cSt (20 °C)
Kinematic viscosity	ASTM 445	45 cSt (99 °C)
Viscosity index	ASTM 2270	345
Surface tension	Du Nouy	25 dynes/cm (20 °C)
Evaporation rate	ASTM 972	0.1 percent (149 °C)
Average MW	Viscometric	9500

TABLE 2. - METAL AND CERAMIC MATERIALS

1. Stainless steel, type 440-C annealed. QQ-S-763, condition A
2. Copper, alloy number 110, nominal 99.90 percent electrolytic
3. Aluminum alloy, 2024 QQ-A-225/6
4. Titanium alloy, 6Al-4V AMS 4928
5. Iron, pure. "ingot magnetic iron" 99.86 percent
6. Chromium plated carbon steel per AMS 2406. nominal thickness 0.001 in.
7. Brass, yellow C26800
8. Zinc, 99.9 percent
9. Aluminum-oxide ceramic
10. Zirconium oxide ceramic

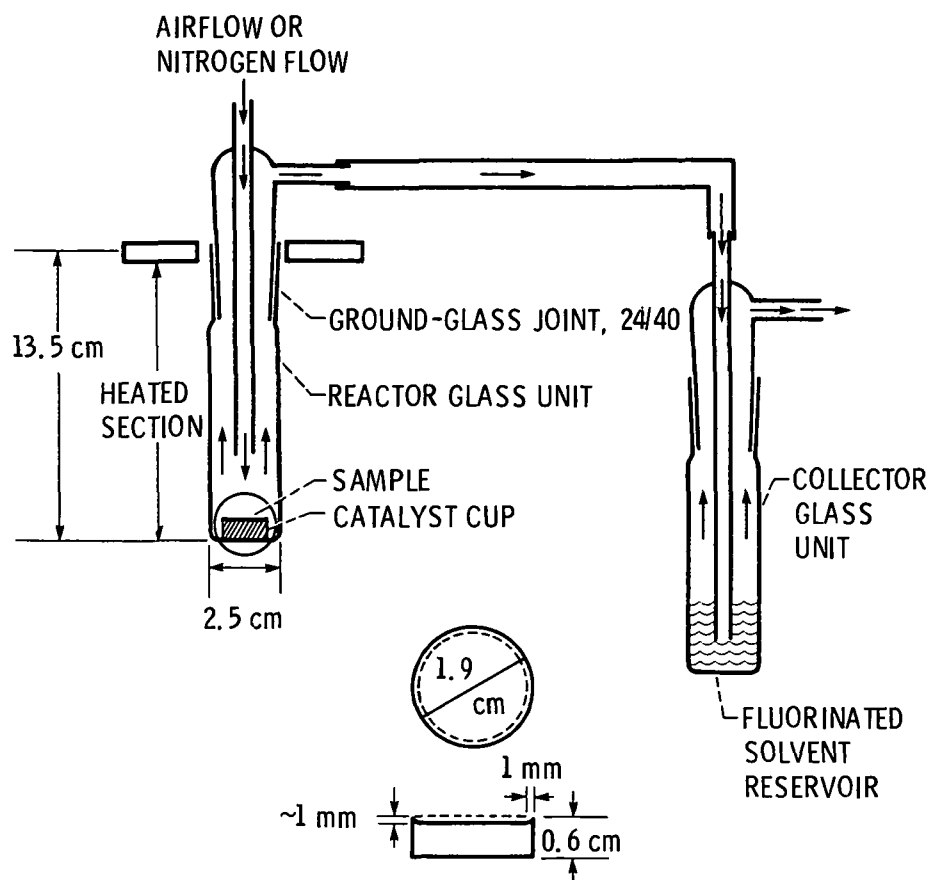


Figure 1. - Thin film oxidation apparatus.

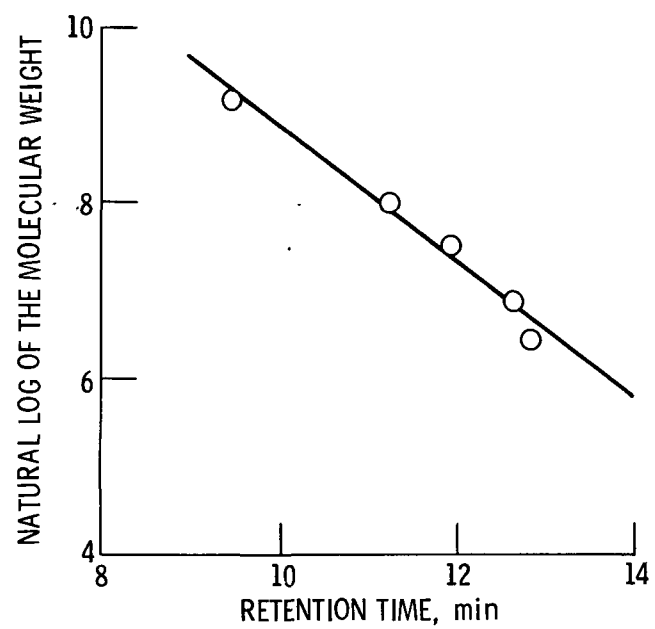


Figure 2. - Molecular weight distribution chart.

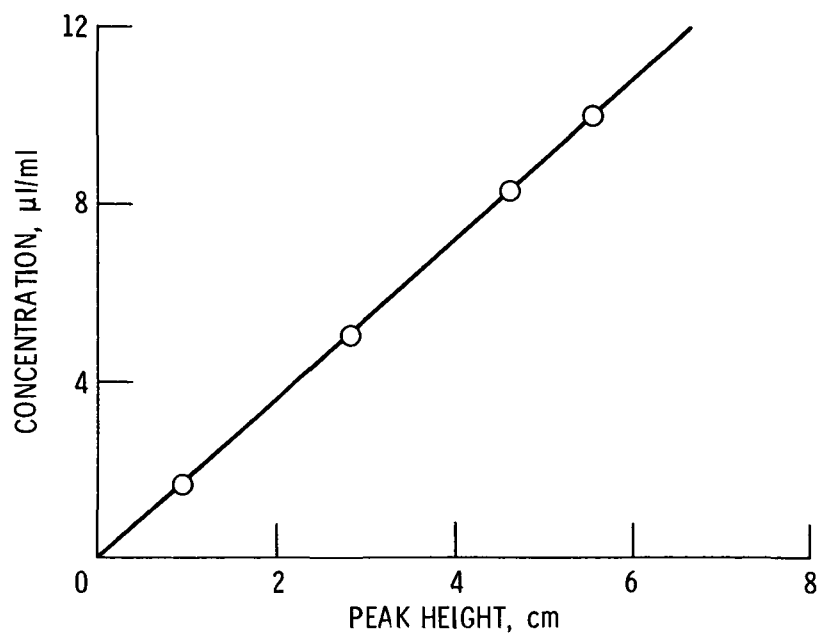
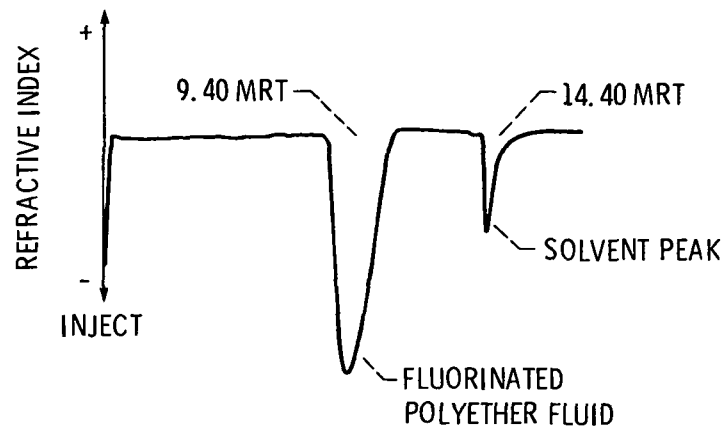
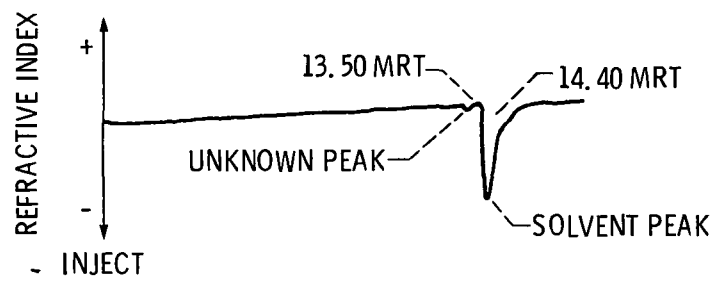


Figure 3. - Concentration chart for the fluorinated polyether sample.





(a) Cup solution.



(b) Gaseous solution.

Figure 4. - 440 C stainless steel specimen chromatographic results.

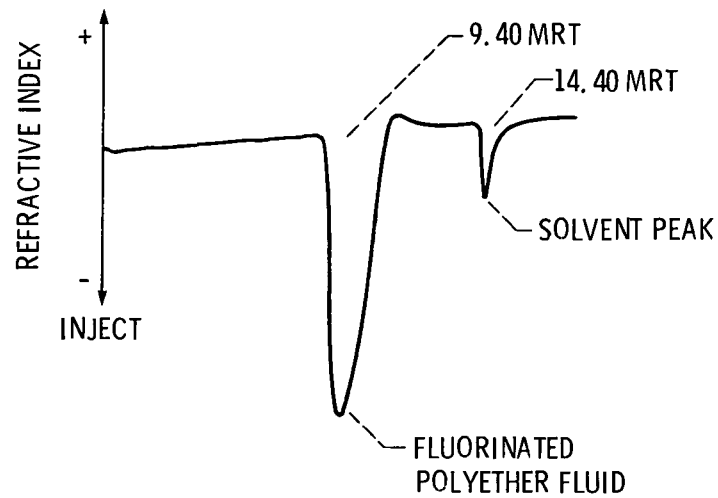
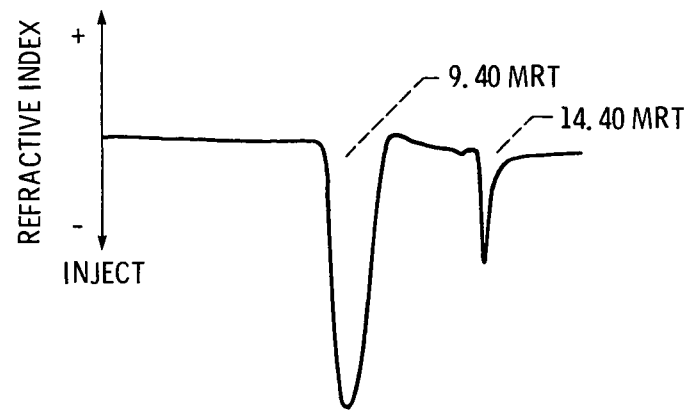
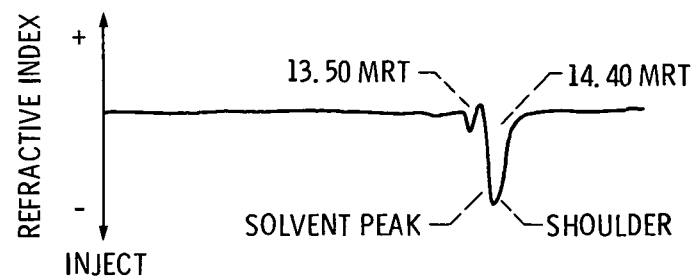


Figure 5. - 440 C stainless steel specimen chromatographic result for thin film test conducted in a nitrogen atmosphere (cup solution).

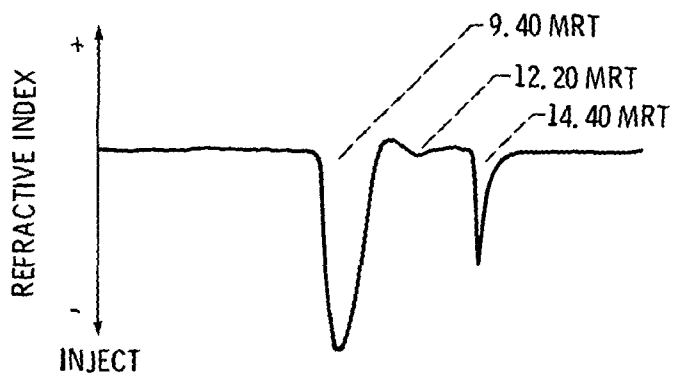


(a) Cup solution.

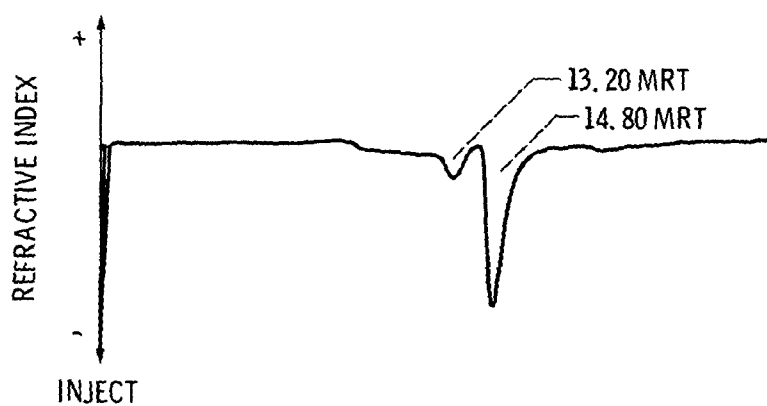


(b) Gaseous solution.

Figure 6. - Pure iron chromatographic results.

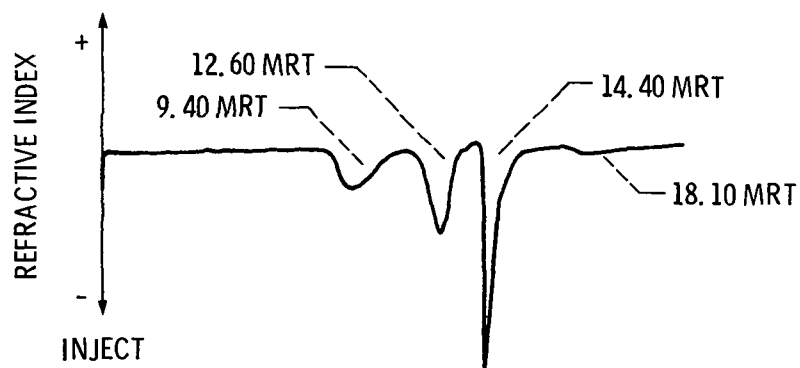


(a) Cup solution.

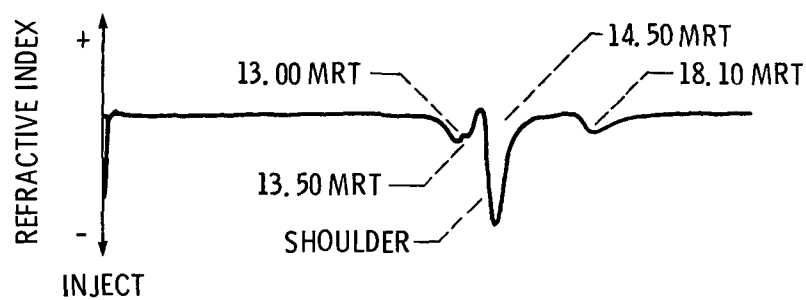


(b) Gaseous solution.

Figure 7. - Chromium plated carbon steel chromatographic results.



(a) Cup solution.



(b) Gaseous solution.

Figure 8. - Titanium alloy chromatographic results.

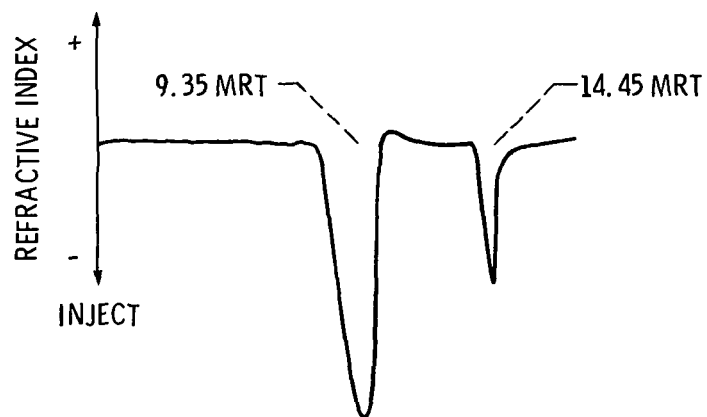


Figure 9. - Titanium alloy chromatographic results for the thin film test conducted in a dry nitrogen atmosphere (cup solution).

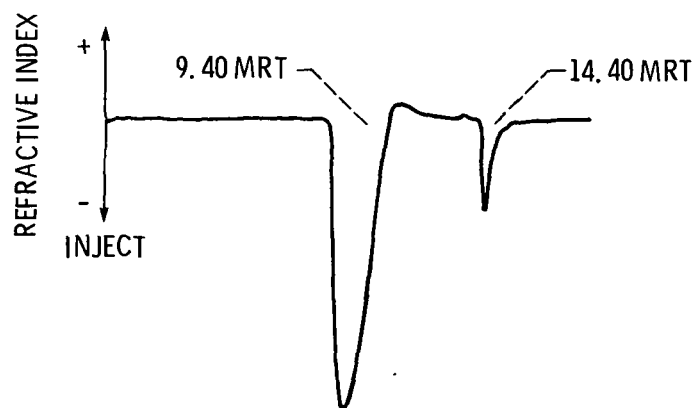
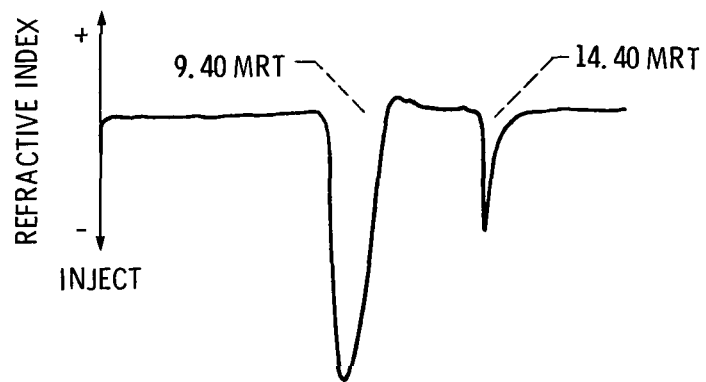
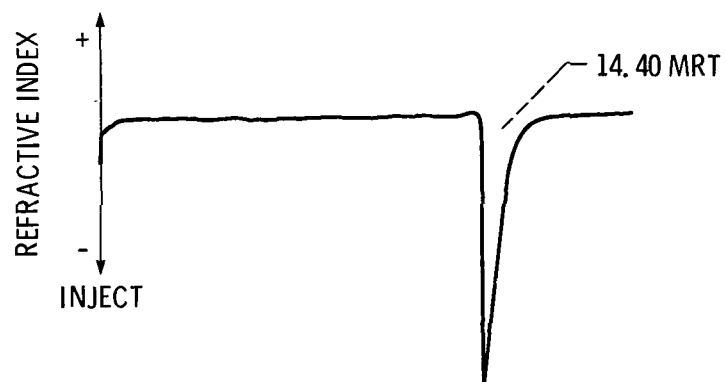


Figure 10. - Copper specimen chromatographic results (cup solution).

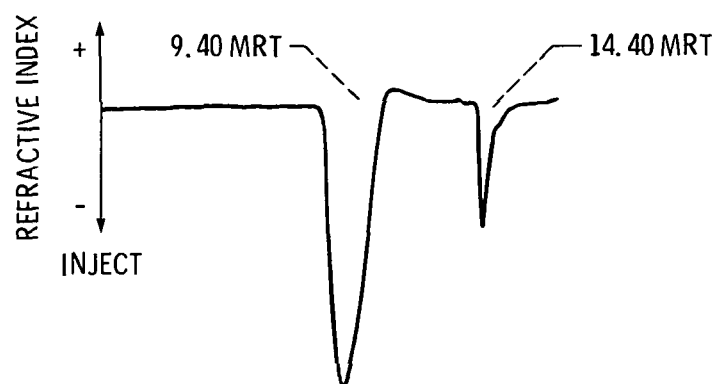


(a) Cup solution.

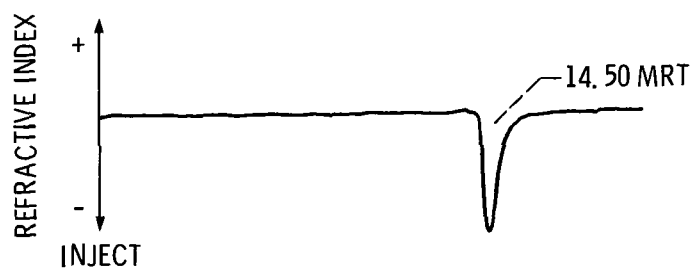


(b) Gaseous solution.

Figure 11. - Zinc specimen chromatographic results.



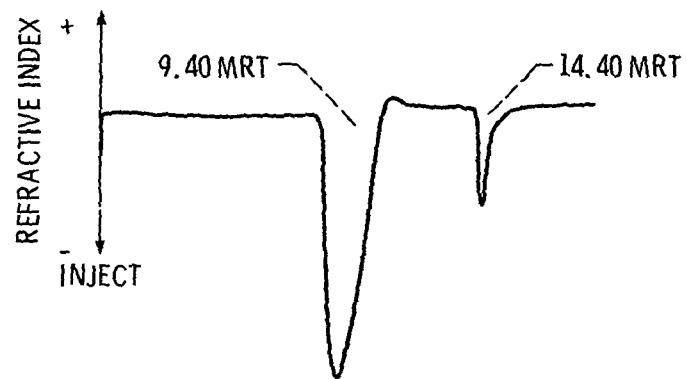
(a) Cup solution.



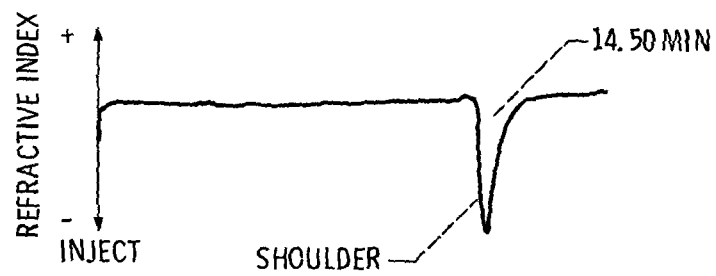
(b) Gaseous solution.

Figure 12. - Brass alloy chromatographic results.



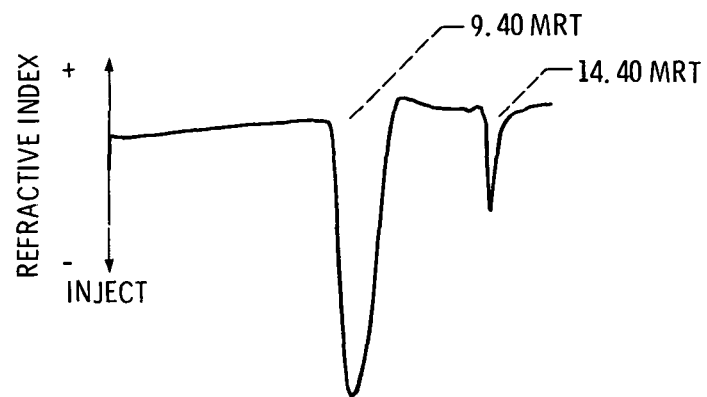


(a) Cup solution.

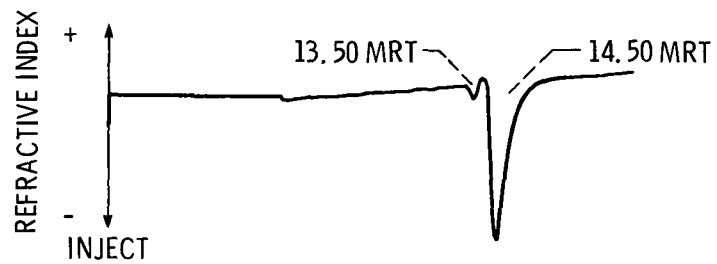


(b) Gaseous solution.

Figure 13. - Aluminum specimen chromatographic results.

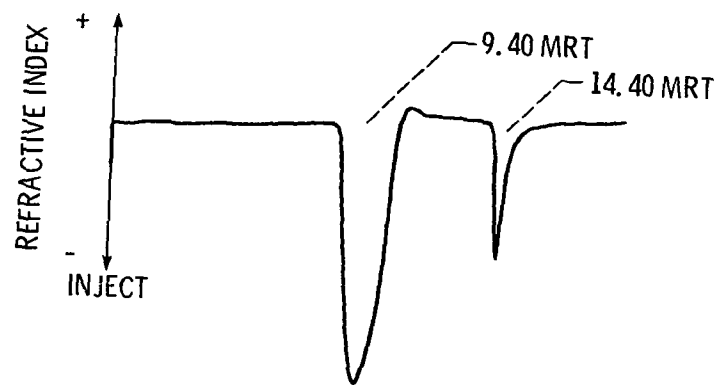


(a) Cup solution.

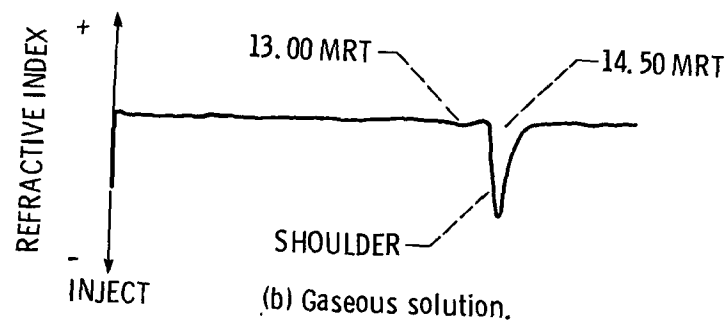


(b) Gaseous solution.

Figure 14. - Aluminum oxide ceramic chromatographic results.



(a) Cup solution.



(b) Gaseous solution.

Figure 15. - Zirconium oxide ceramic chromatographic results.

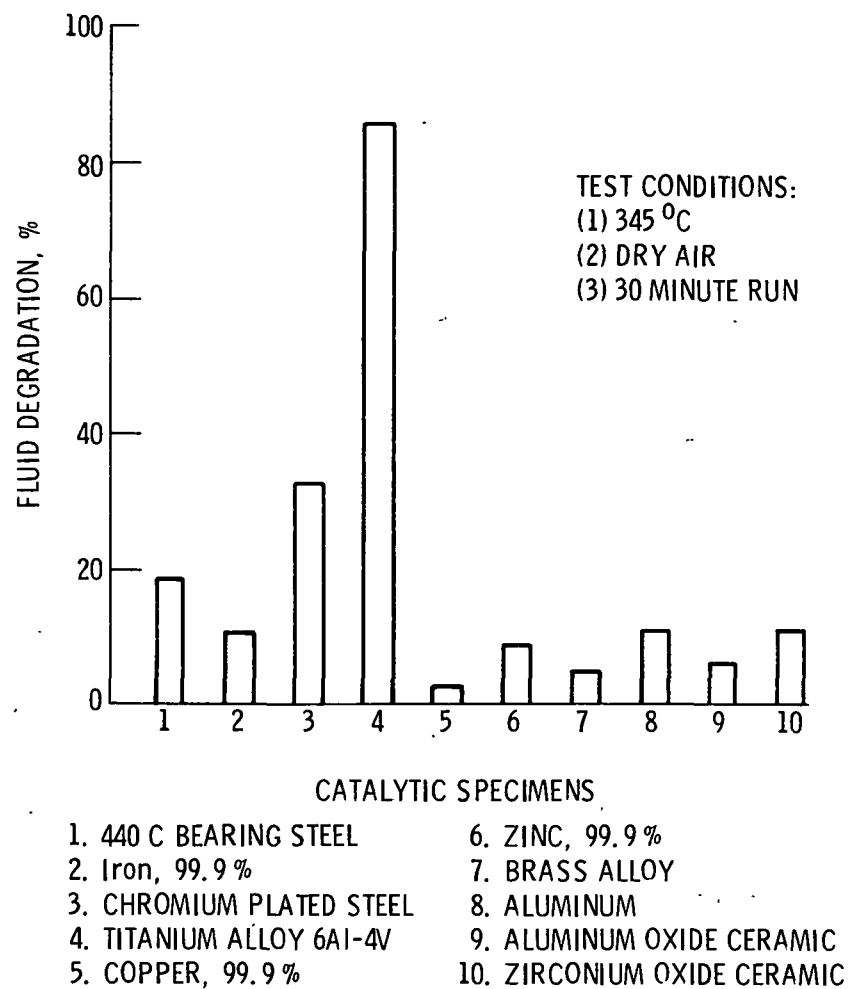


Figure 16. - Thin film catalytic degradation of a fluorinated polyether fluid - a candidate high-temperature liquid lubricant.

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